AD-A086 691 ROCKWELL INTERNATIONAL ANAHEIM CA ELECTRONICS RESEAR--ETC F/G 7/4
INVESTIGATION OF ELECTROCHROMIC DIPHTHALOCYANINES.(U)
JUN 80 M M NICHOLSON, R V GALIARDI F49620-79-C-0104
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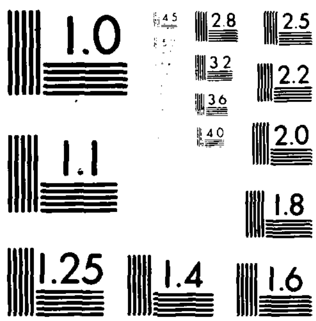

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INVESTIGATION OF ELECTROCHROMIC DIPHTHALOCYANINES

LEVEL II

Electronics Research Center
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June 1980

Final Report for Period 1 April 1977 to 31 March 1980

Contracts F49620-77-C-0074 and F49620-79-C-0104

Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling Air Force Base, D. C. 20332

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR-80-0536	2. GOVT ACCESSION NO. AD-A086 691	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) INVESTIGATION OF ELECTROCHROMIC DIPHTHALOCYANINES		5. TYPE OF REPORT & PERIOD COVERED Final, 1 April 1977 – 31 March 1980
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. M. Nicholson, R. V. Galiardi, F. A. Pizzarello, G. A. Layman		8. CONTRACT OR GRANT NUMBER(s) F49620-79-C-0104; F49620-77-C-0074
9. PERFORMING ORGANIZATION NAME AND ADDRESS Electronics Research Center, Rockwell International, Anaheim, CA 92803		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B2
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NC, Bolling Air Force Base, DC 20332		12. REPORT DATE June 1980
		13. NUMBER OF PAGES 76
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electrochromism; Phthalocyanines; Rare earths; Electrochemistry; Kinetics		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See other side.		

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20. ABSTRACT

Lanthanide diphthalocyanine films on tin oxide electrodes in contact with aqueous electrolytes exhibit a series of color changes on variation of the applied potential. ~~These~~ systems are of special interest because of their unusual electrochemistry and their ~~potentialities~~ for electrochromic display applications. In this project, the electrochromism of lutetium diphthalocyanine films was investigated by several experimental approaches. The results confirmed that the color changes were due to faradaic reactions rather than temporary field effects. They provided information on the stoichiometry and kinetics of the electrode processes and on the stabilities of color-converted forms of the dye.

The lutetium diphthalocyanine film was initially green. By simple chemical and electrochemical diagnostic experiments, it was found that a blue cathodic product formed with utilization of hydrogen ion. The blue material was converted to green by reaction with oxygen. Anodic reactions could produce more than one red form of the dye, generally without a pH change in the electrolyte. The red materials were strong oxidizing agents. Thin-layer electrochemical measurements confirmed the participation of protons in the cathodic process. The thin-layer cell design, which included a shallow, precisely etched glass cavity, may prove useful in other research.

A complementary solid-state electrochemical investigation of lutetium diphthalocyanine in this laboratory led to the proposal that anodic oxidation occurred by rapid migration of anions from the electrolyte into the solid organic film. This mechanism was independently verified in the present work by radiotracer experiments using chloride and sulfate electrolytes. The results showed, approximately, that two electrons were lost per molecule of diphthalocyanine converted from green to red.

The kinetics of the anodic dye reaction on tin oxide in 1 M KCl was investigated by a galvanostatic transient technique, with simultaneous monitoring of the optical transmission of the film. At current densities of 0.3 to 6 mA/cm^2, the rate was controlled by an ionic space charge in the red oxidation product. Interpretation of the data by space-charge theory yielded a dielectric constant of approximately 10 for the red material.

Some of the red films gradually reverted to green on standing. The faded films were still convertible to the usual series of colors, however, by reactivation in the electrochemical cell. The rates of these chemically-produced color changes in chloride-containing films on tin oxide in ambient air were measured spectrophotometrically at temperatures from 25 to 60°C. A related, but more detailed, study was made on sapphire-supported films with electrolytes containing different anions. In that case, the red films were produced anodically by propagation of the red/green boundary upward from the liquid surface toward the electronic contact. The fading reactions in moist air followed first-order kinetics with respect to the red dye species. Three types of behavior were characterized: (a) low-voltage color propagation and relatively fast return from red to green ($k \approx 0.1\ hr^{-1}$) (OAc^- and F^-); (b) higher-voltage propagation and little or no fading ($k \leq 0.003\ hr^{-1}$) (Cl^-, Br^-, and $SO_4^{=}$); and (c) no color propagation (I^- and ϕCOO^-).

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FIGURES

I. INTRODUCTION

The lanthanide diphthalocyanines have a sandwich structure in which the trivalent rare-earth ion is located between two phthalocyanine rings. The formula may be written $MH(Pc)_2$ to indicate the presence of a labile hydrogen within the molecular unit. Moskalev and Kirin first reported that a film of such a compound on a tin oxide substrate underwent a remarkable series of color changes when subjected to various applied potentials in an aqueous electrolyte.(1) Lutetium diphthalocyanine is initially green. The Soviet investigators suggested that the reddish color produced in this film at anodic potentials was due to complexing with oxygen or water, and that the blue or blue-green color at cathodic potentials resulted from ionization to $Lu(Pc)_2^-$ and H^+ under the influence of the applied field.(2)

In subsequent work at Rockwell International, which was oriented toward display applications,(3,4) it became evident that these mechanisms did not fully account for the electrochromic behavior. Charge densities equivalent to one or two electrons per molecule were found to be involved in both anodic and cathodic processes. Moreover, the colors remained after the electrical excitation was removed. Hence, the color changes appeared to result from faradaic reactions rather than field effects.

This project with the Air Force Office of Scientific Research was undertaken to determine reaction mechanisms and kinetics in the electrochromic diphthalocyanines. Vacuum-sublimed films of lutetium diphthalocyanine were investigated in several aqueous electrolytes by a variety of experimental techniques. The approaches included: Electrochemical measurements by linear potential-sweep voltammetry in thin-layer cells and by galvanostatic transients; radiotracer experiments; absorption spectroscopy in the visible region; and a number of chemical diagnostic tests. A solid-state color-boundary propagation technique developed in a related project* sponsored by the Office of Naval Research was also employed to produce color-converted films on insulating substrates.

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*Contract N00014-77-C-0636

Results of the tracer investigation and the electrode kinetics study by galvanostatic transients were published in scientific journals. They are presented here in abstract form. Unpublished work on chemical diagnostics, thin-layer electrochemistry, and chemical kinetics of color changes in anodically oxidized dye films is reported in more detail. The investigation of diphthalocyanine electrode processes is continuing under Air Force Contract F49620-80-C-0060.

II. STATEMENT OF WORK

a. Measure and correlate electrochemical and spectroscopic characteristics of rare-earth diphthalocyanine films on transparent conductive substrates.

b. Interpret and describe the fundamental processes occurring in these materials under electrical excitation.

c. Determine effects of electrolyte composition on the electrode reactions.

d. Determine the time dependence of electrochemical and optical-absorption characteristics of diphthalocyanine films in contact with aqueous electrolytes for intervals in the range of 100 to 0.01 milliseconds.

e. Analyze the data on the basis of kinetic models to obtain quantitative descriptions of the electrochromic processes.

III. RESULTS

A. DIAGNOSTIC EXPERIMENTS*

Diagnostic experiments were performed with lutetium diphthalocyanine by a variety of simple chemical and electrochemical procedures. Qualitative observations on the oxidized and reduced forms of the dye are summarized in Tables 1 and 2. As expected, products within the blue range were sensitive to oxygen, and protons were utilized in their formation. Red products were formed anodically in several electrolytes or by direct reaction of the green dye with chlorine. Anodic oxidation could occur without a pH change in the solution. The visible absorption spectrum of the red film produced anodically in KCl resembled very closely that of the red formed in dry chlorine. The red products were strong oxidizing agents; they could be converted back to green by reaction with hydrogen peroxide. It was concluded from these early experiments that several forms of red dye material could exist. The one produced in a KCl electrolyte faded toward green when placed in a vacuum; it apparently contained a volatile component.

B. THIN-LAYER ELECTROCHEMISTRY

Thin-layer electrochemistry[5] should offer a very sensitive approach for quantitative investigation of the diphthalocyanine electrode reactions. With this technique, the dye film on a transparent conductor can form one wall of a thin electrolyte-filled cavity, while an inert electrode such as gold forms the opposite wall. Reference and counter electrodes are located in the bulk of the solution outside the cavity. The dye can be converted electrochemically from one color state to another while in the cavity. Soluble species such as H^+ or O_2, which may be involved in the electrochromic reactions, are determined voltammetrically at the inert electrode. Since the cell thickness is typically in the range of 5 to 50 μm, monolayer quantities of electroactive species are easily measured. In a variation of the technique, a soluble reactant may be generated coulometrically at the inert electrode and then utilized in the dye reaction.

*Unpublished

TABLE 1

CHEMISTRY OF RED PRODUCT(S) OF LUTETIUM DIPHTHALOCYANINE

Observations	Inferences
Formation	
Red material forms by anodic reaction of green $LuH(Pc)_2$ in KCl, K_2SO_4, or NaOAc.	One or more red faradaic oxidation products
Direct chemical reaction of green dye with wet or dry Cl_2.	A red form may contain chorine; this reaction does not require water.
Stability in Air	
Red formed in KCl(on SnO_2 substrate) changes to dull green in $\sim$1 hr at 60°C.	SnO_2 may be involved in gradual fading of red to green.
Red formed in NaOAc changes to bright green in air within 2 hr.	
Behavior in Vacuum or Helium	
Fades to lighter red.	Volatile component may be lost; Cl_2, O_2, or (in some cases) H_2O.
Confinement in Thin Electrolyte Layer	
Red fades to green in electrolyte layers $\sim$ 4 to 100 μm thick.	Not yet understood; can occur in red film on SnO_2 or Al_2O_3 substrate.

TABLE 1 (CONTINUED)

CHEMISTRY OF RED PRODUCT(S) OF LUTETIUM DIPHTHALOCYANINE

Observations	Inferences
Direct Reactions	
H_2O_2 converts red to green.	Red form is a strong oxidizing agent.
0.1 M NaOH converts red to green in about 1 min.	
Electrochemical Reactions	
Red is cathodically converted to green--usually without pH change.	More than one red product may exist.

TABLE 2

CHEMISTRY OF BLUE OR GREENISH-BLUE PRODUCT(S) OF LUTETIUM DIPHTHALOCYANINE

Observations	Inferences
Formation	
Blue material forms by cathodic reduction of green $LuH(Pc)_2$; solution becomes alkaline.	Greenish-blue form probably requires at least 1 electron; deep blue may be nonstoichiometric.
Blue is formed by shorting green dye electrode to pre-cathodized SnO_2 in KCl.	A reducing agent such as $H^{\cdot}$ is stored in cathodized SnO_2.
Stability in Air	
Blue dye turns green in air; reaction is faster in acidic solutions.	Blue form is an active reducing agent.
Behavior in Helium	
Stable for days on SnO_2 or Al_2O_3 substrate in dry atmosphere.	

1. Investigation of Lutetium Diphthalocyanine*

In the first year of this project, a limited effort was made to investigate lutetium diphthalocyanine by thin-layer linear-potential-sweep voltammetry. This was partially successful. Difficulties arose from subsidiary electrochemical processes on the tin oxide substrate, from occasional contamination of the gold-plated detector electrode, and from a peculiar tendency of the red dye to revert to green when confined in the cavity. The first two limitations probably can be overcome with modified cell structures and materials, and the spontaneous color change in narrow spaces could prove to be of further interest.

Nowithstanding these problems, it was demonstrated by thin-layer voltammetry that hydrogen ions were released in the anodic oxidation of the blue dye. To verify the technique, measurements were made on a known H^+ solution with a plain glass cell wall and then with a bare tin oxide wall. Details of the cell structure are given in Part 2 of this section. Figure 1 shows potential-sweep voltammograms for hydrogen ion on the gold electrode at pH 3.00 in 1 M KCl. Coulometric data for the combined areas under the peaks of the first and second scans (corrected for background) are included in Table 3. Data for the known solution were satsifactory, and no interference occurred when the opposite cell wall consisted of tin oxide that had not been treated electrochemically.

With dye/tin oxide electrodes that had been subjected to potential pulses, the results were less consistent. Blue films, formed externally and pulsed to red** inside the cavity, occasionally produced excellent hydrogen reduction peaks at the detector electrode, as in Figure 2(a). Further experiments of this type were less satisfactory, however. The problem apparently was due to contamination of the gold electrode--possibly by organic material from the polyimide insulator on the gold

*Unpublished

**The blue-to-green transition was somewhat difficult to control under the conditions of these experiments.

Conditions: 1.6 x 10^{-3} M HCl in 1 M KCl; gold detector electrode, 0.713 cm^2 area; cell thickness 49 μm; sweep rate 10 mV/sec.

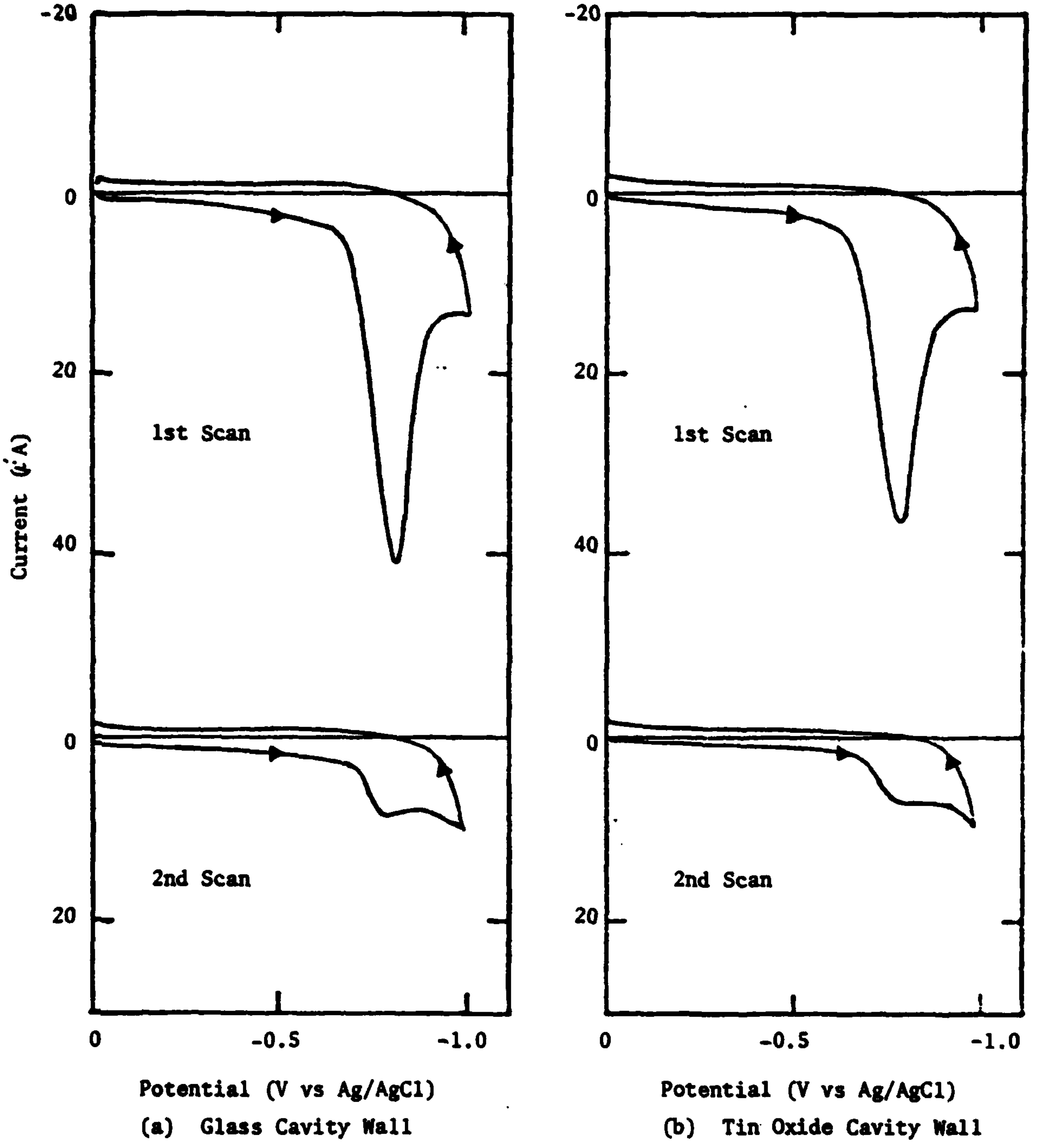


Figure 1. Cyclic Voltammograms for Hydrogen Ion in Thin-Layer Cells

TABLE 3

COULOMETRIC DETERMINATIONS OF HYDROGEN ION WITH GOLD ELECTRODE IN THIN-LAYER CELL[a]

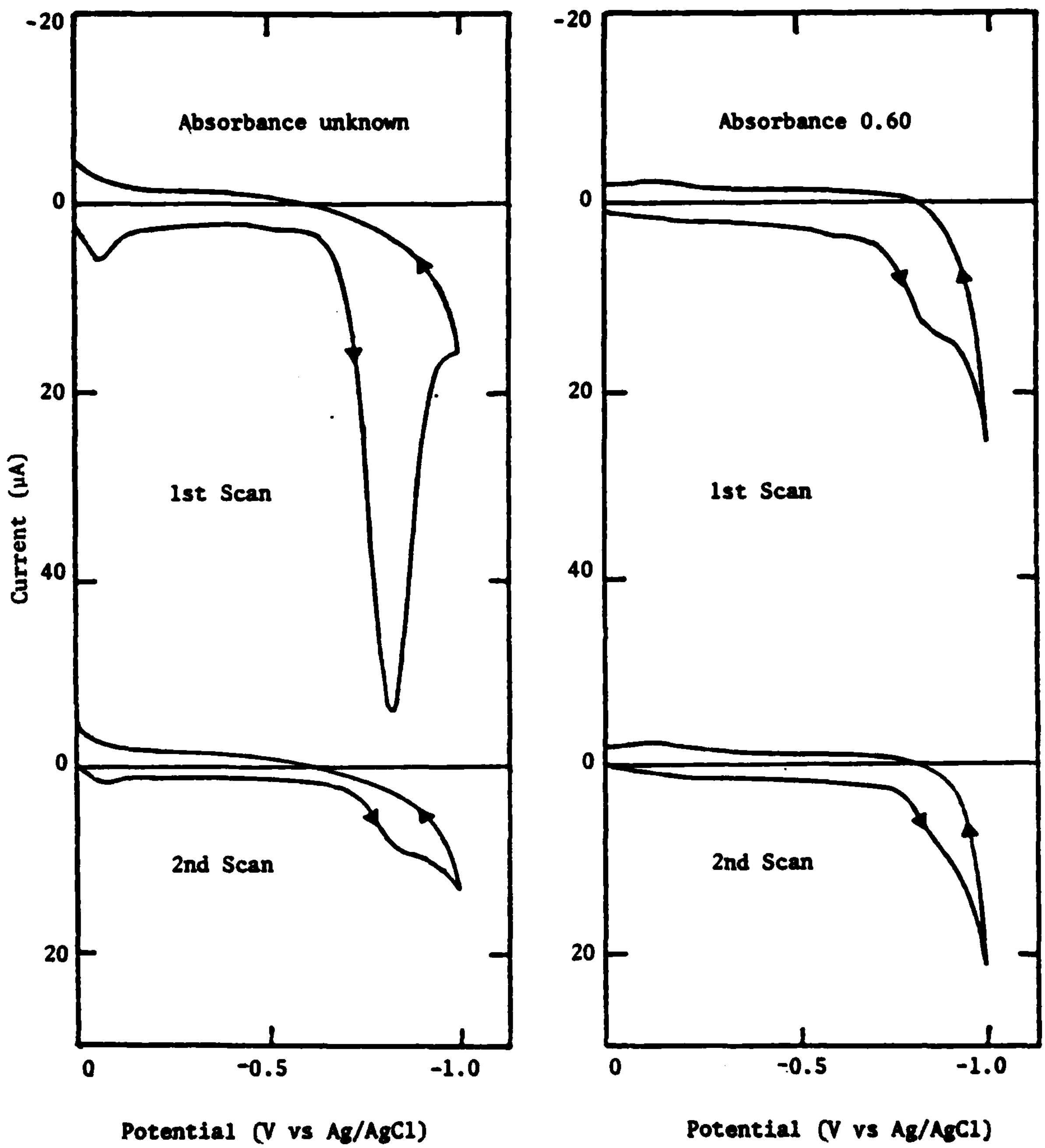
Cell Wall	Source of H^+	Moles $H^+ \times 10^9$		Apparent n	Comments
		Calculated	Found		
Glass	HCl	5.8	5.6	- -	Figure 1(a).
SnO_2	HCl	5.8	5.8	- -	Figure 1(b).
		5.8	5.9	- -	
Dye/SnO_2	Blue-to-Red Transition				
Absorbance Unknown		- -	6.4	- -	Well defined peak, Figure 2; absorbance of 0.4 calculated for n = 2.
0.60		- -	2.1	0.40	Distorted curve, Figure 2[c]
0.86		- -	0.9	0.13	Poorly formed.[c]
0.92		- -	1.8	0.22	Poorly formed.[c]

[a]Conditions: Gold-plated electrode, 0.713 cm^2 area; cavity thickness 45.9 μm; 1 M KCl; sweep rate 10 mV/sec.

[b]Optical density (absorbance) of initial green film at maximum near 665 nm.

[c]Small H^+ reduction currents; gold surface apparently contaminated.

Conditions: Electrolyte 1 M KCl; gold detector electrode, 0.713 cm^2 area; cell thickness 49 μm; sweep rate 10 mV/sec; blue dye converted to red at 1.0 V in cavity.



(a) Clean Gold Electrode

(b) Gold Electrode Probably Contaminated

Figure 2. Cyclic Voltammograms in Thin-Layer Cells Following Blue-to-Red Transition of Lutetium Diphthalocyanine

electrode lead, or from the dye film itself. A contaminated gold electrode produced distorted or very small hydrogen-reduction curves such as that of Figure 2(b). The corresponding n values for the dye reaction seemed much too low, as reported in Table 3. Additional data for cleaner gold electrodes were needed to determine accurately the number of protons involved.

The participation of protons in the reduction scheme was confirmed independently by placing a flat-ended glass electrode next to the dye film while the color was being changed in large potential steps. Repeated pulsing between the blue and red states with air absent was accompanied by swings to pH levels of about 10 and 4, respectively. Corresponding tests on blank tin oxide showed essentially no pH variations. Pulsing between green and red in air-free KCl also occurred without a pH change. Hence, protons were consumed in the green-to-blue conversion.

Further quantitative work on the dye films by thin-layer electrochemistry was postponed because other techniques were showing greater promise of near-term results.

2. Thin-Layer Cell Design*

Since the cell design developed for this work may find other applications in thin-layer electrochemistry, it will be described in some detail. The primary feature was the use of a precision-etched glass cavity rather than a separate spacer such as a plastic strip to define the thickness of the electrolyte layer. Precise etching of shallow cavities in glass is a very old process.[6] It was employed more recently for construction of liquid-crystal cells,[7] but the application to thin-

*Publication planned.

layer electrochemistry appears to be new. Advantages are precision and permanence of the spacing, and ease of cleaning and reassembling the cell.

The thin-layer cell structure is illustrated in Figure 3. For the dye experiments, the flat plate was an electrochromic specimen. In other instances, it was plain glass. The cavity plate, including the inert metal electrode, was constructed from a microscope slide by means of photomasking techniques. The cell assembly was secured by a rubber band for easy replacement of the electrodes or the electrolyte.

Principal steps in fabrication of the cavity plate were as follows:

1. A glass cavity was etched through a chromium in-contact mask with an etchant consisting of 1 volume of 49% HF plus 1 volume of water. The surface was brushed manually during etching to prevent accumulation of silicon fluoride.

2. A vacuum-evaporated chromium-platinum electrode disk with its electrical lead strip was fabricated in the cavity by conventional photodelineation procedures. The metal was 0.2 μm platinum on top of 0.02 μm chromium.

3. The metal lead was insulated with photodelineated polymide.

4. The exposed metal was electroplated with ~0.5 μm gold, when necessary, to avoid acid attack at the edges of the chromium underlayer, or to provide a working surface of gold.

The profile of an etched cavity determined with a Dektak profilometer is shown in Figure 4. The depth was 45.9 ± 0.3 μm. The cavity wall, 1.25 cm wide, was very smooth, and the corners were well formed. Figure 5 shows that the etching rate was constant after the first 1.5 min. Hence, it was possible to produce cavities with closely specified thicknesses, once this plot was established. The electrolyte channels connecting the platinum electrode region with the other part of the cell had the same thickness as the cavity. By weighing two unetched microscope slides

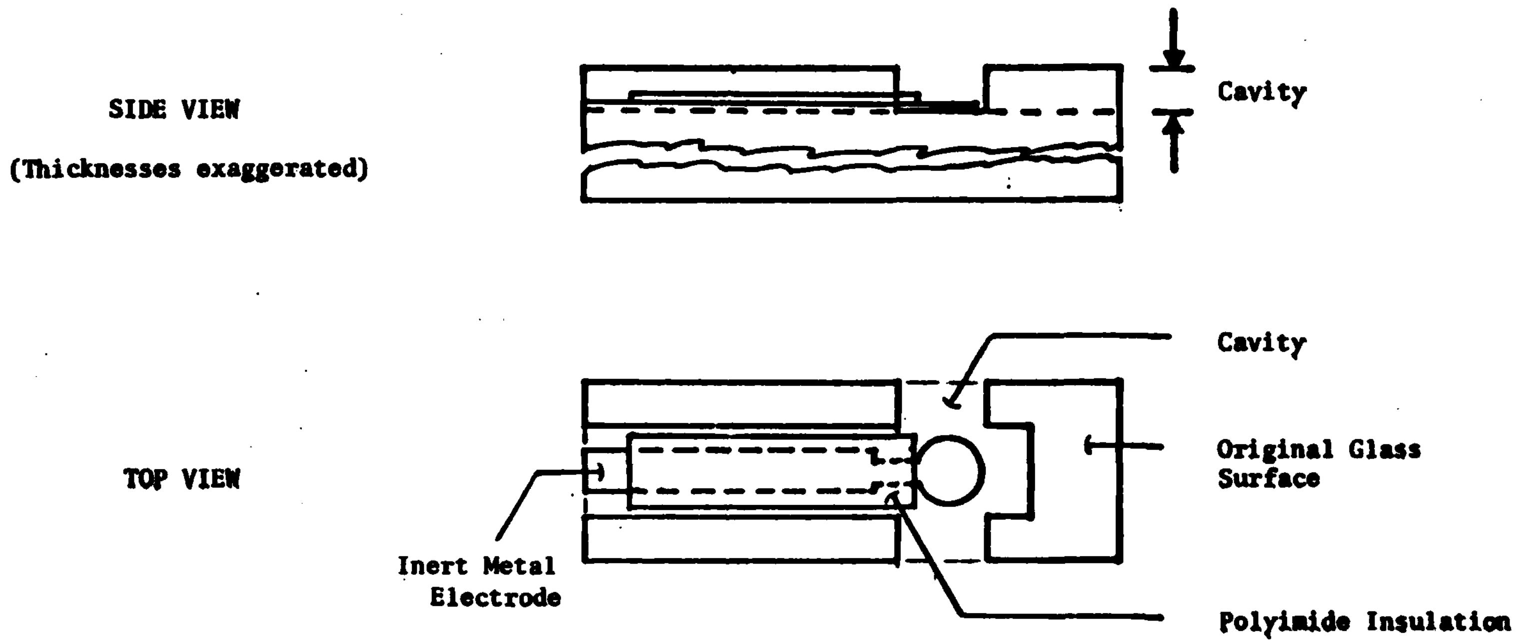


Figure 3. Thin-Layer Electrochemical Cell

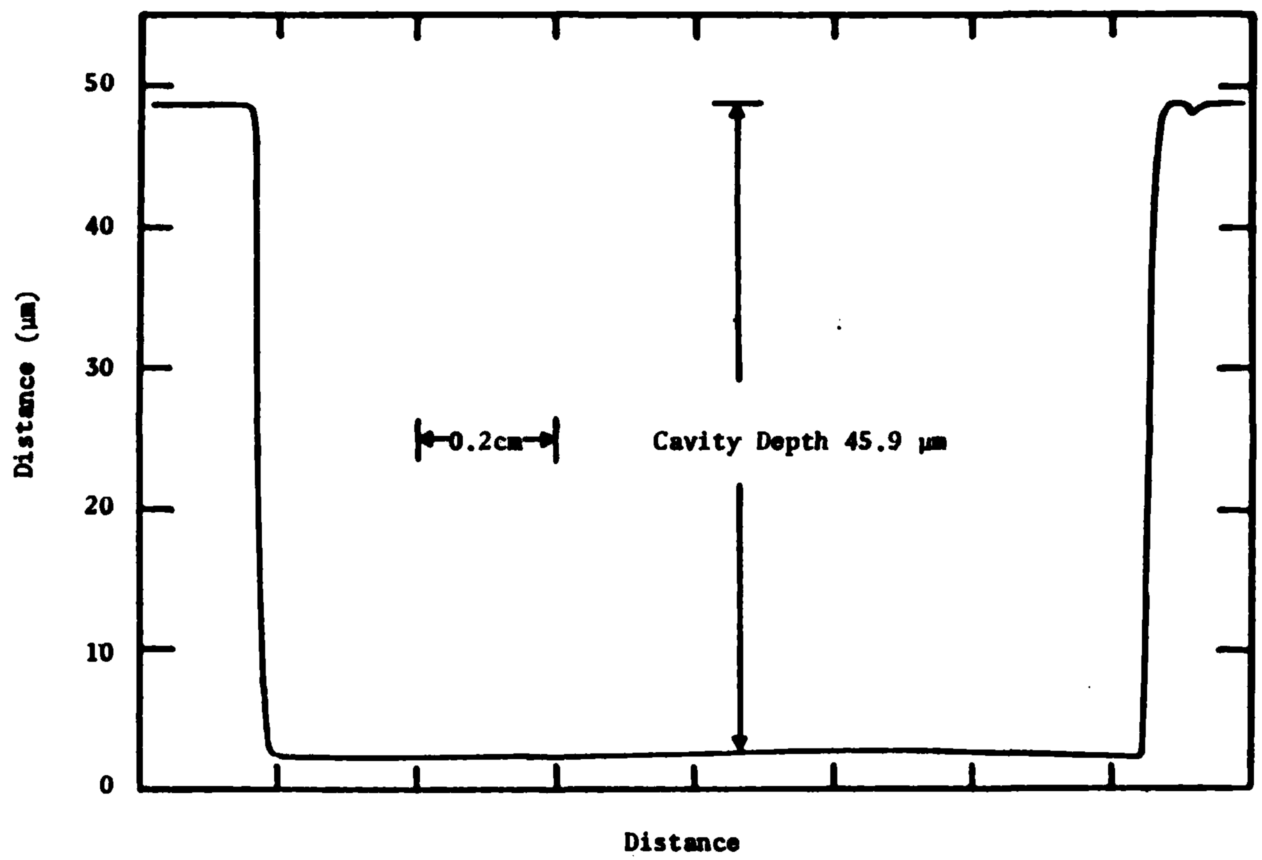


Figure 4. Profile of Cavity Etched in Glass

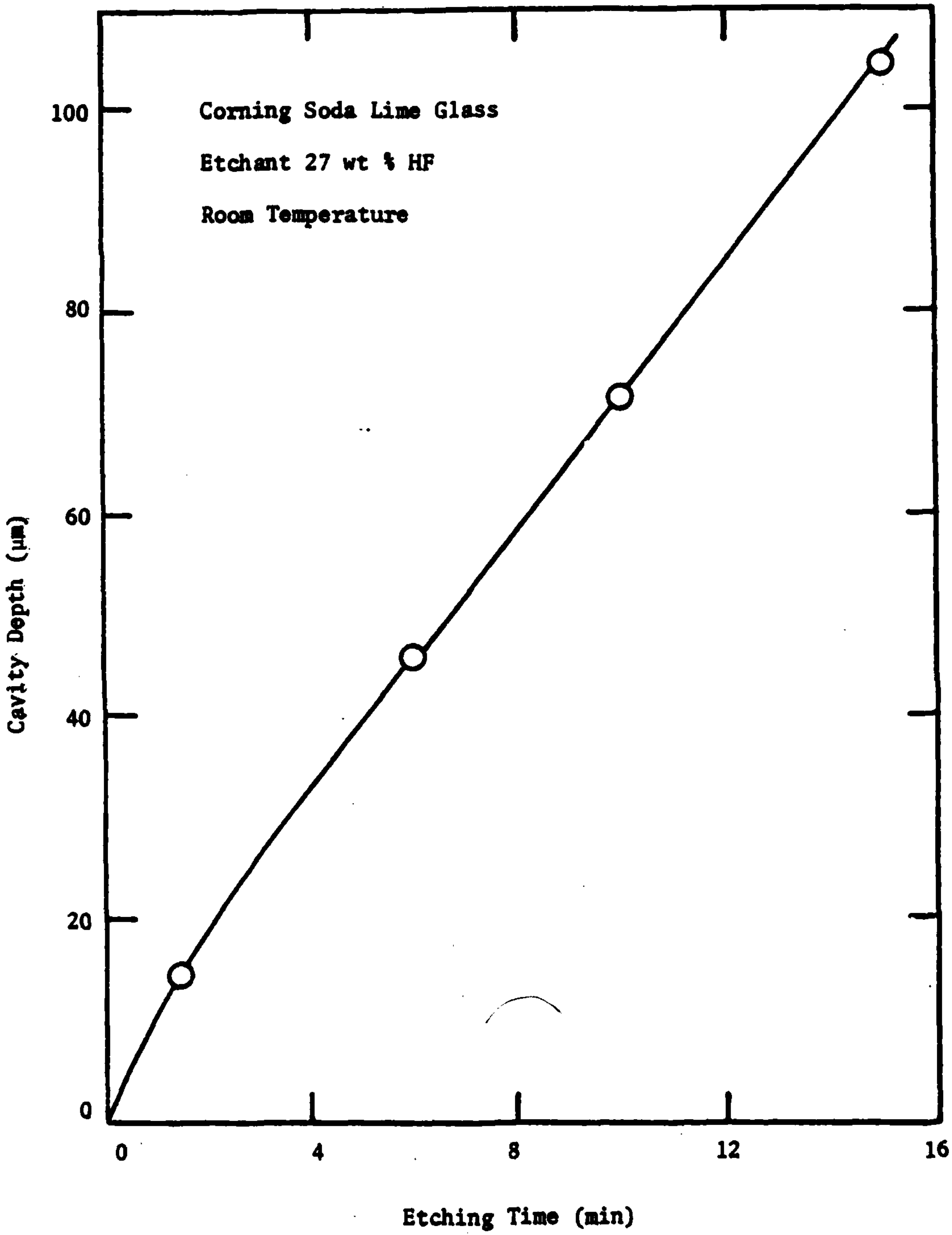


Figure 5. Dependence of Cavity Depth on Etching Time

pressed together, with a film of water between, it was determined that the liquid film in the area of close contact was about 4 μm thick. This liquid thickness in the "glass-to-glass" areas around the cavity will vary slightly with the flatness of the plates and pressure upon them. Uncemented cells will therefore be more useful at relatively large electrolyte thicknesses. At 25 μm, for example, the error due to variations in the contacting liquid film should not exceed ∿ 4%.

The electrochemical responses of 49-μm cells were verified from measurements on 1 mM $K_3Fe(CN)_6$ in 1 M KCl by cyclic voltammetry and potential-step coulometry. The results are summarized in Table 4.

TABLE 4

VERIFICATION OF THIN-LAYER CELL RESPONSES WITH $K_3Fe(CN)_6$[a]

A. CYCLIC POTENTIAL-SWEEP VOLTAMMETRY[b]

Charge (mC)			Peak Current (μA)		
Measured		Calculated	Measured		Calculated (5)
Anodic	Cathodic		Anodic	Cathodic	
0.33	0.33	0.34	27.8	29.1	32

B. POTENTIAL-STEP COULOMETRY[c]

Charge (mC)		
Measured		Calculated
Anodic	Cathodic	
0.31	0.30	0.34

[a]Platinum electrode, 0.713 cm^2 area; cavity thickness 45.9 μm; solution 10^{-3} M $K_3Fe(CN)_6$ in 1 M KCl.

[b]Sweep rate 10 mV/sec.

[c]Potential stepped between 0.500 and 0.075 V vs Ag/AgCl.

C. RADIOTRACER STUDY: SOLID-STATE ANION MIGRATION IN THE ANODIC OXIDATION OF LUTETIUM DIPHTHALOCYANINE[8]

Abstract

The solid-state anion-migration mechanism proposed recently to account for the results of moving-boundary measurements on lutetium diphthalocyanine films was confirmed by quantitative radiotracer experiments using chloride and sulfate electrolytes. The same mechanism was independently demonstrated for these anions and for bromide by semiquantitative energy-dispersive x-ray spectroscopy. The red oxidation product containing chloride ion decomposed gradually in ambient air, while that containing sulfate or bisulfate appeared to be stable.

D. ELECTRODE KINETICS: GALVANOSTATIC TRANSIENTS IN LUTETIUM DIPHTHALOCYANINE FILMS [9]

Abstract

The anodic oxidation of lutetium diphthalocyanine films on tin oxide in 1M KCl was investigated by a galvanostatic transient technique. The reaction was monitored by simultaneous measurement of the optical transmission. At current densities of 0.3-6 mA/cm^2, the kinetics was controlled by an ionic space charge in the red oxidation product. A dielectric constant of 10 was estimated for this material, using the solid-state mobility of the chloride ion determined in a previous moving-boundary study.[10]

E. CHEMICAL KINETICS OF COLOR CHANGES IN OXIDIZED FILMS

1. Dry Chloride Films on Conductive Tin Oxide*

On removal from the electrochemical cell, the red films from a chloride electrolyte gradually changed toward brownish tones. Heating accelerated conversion to olive green, which was less bright than the original green of the vacuum deposited dye. Such faded films were still convertible to the usual series of colors, however, when reactivated in the cell. The detailed visual effects in the red-to-brown region varied somewhat with the roughness of the tin oxide substrate. These chemical changes and their temperature dependence were investigated in a brief preliminary study described below.

Lutetium diphthalocyanine films on tin oxide were converted to the red form by anodic excitation in air-saturated cells containing 0.1 M KCl. The dye deposit, which occupied a circular area of 0.713 cm^2, was surrounded by a larger area of bare tin oxide. After the color conversion, the specimens were removed from the cell, washed, and dried several minutes room temperature. The "initial red" spectrum was then recorded. A specimen from a set of four replicates was heated in air for successive periods at 40, 50, or 60°C (±5°). At the end of each heating period, the sample was removed from the oven, and its spectrum was again recorded at room temperature. The reaction was quenched by cooling, but the spectral changes could not be monitored during the first 15 min after the specimen was removed from the electrochemical cell.

Figure 6 shows the spectral changes that occurred on standing in air at 60°C. For comparison, spectra recorded in the electrolyte under continuously applied potentials are included in the lower part of the figure. In the present work, the red material was formed at 1.3 V vs Ag/AgCl. By the time the first dry-film spectrum was recorded in air, the curve closely resembled the in situ spectrum at 1.0 V [Curve (g)].

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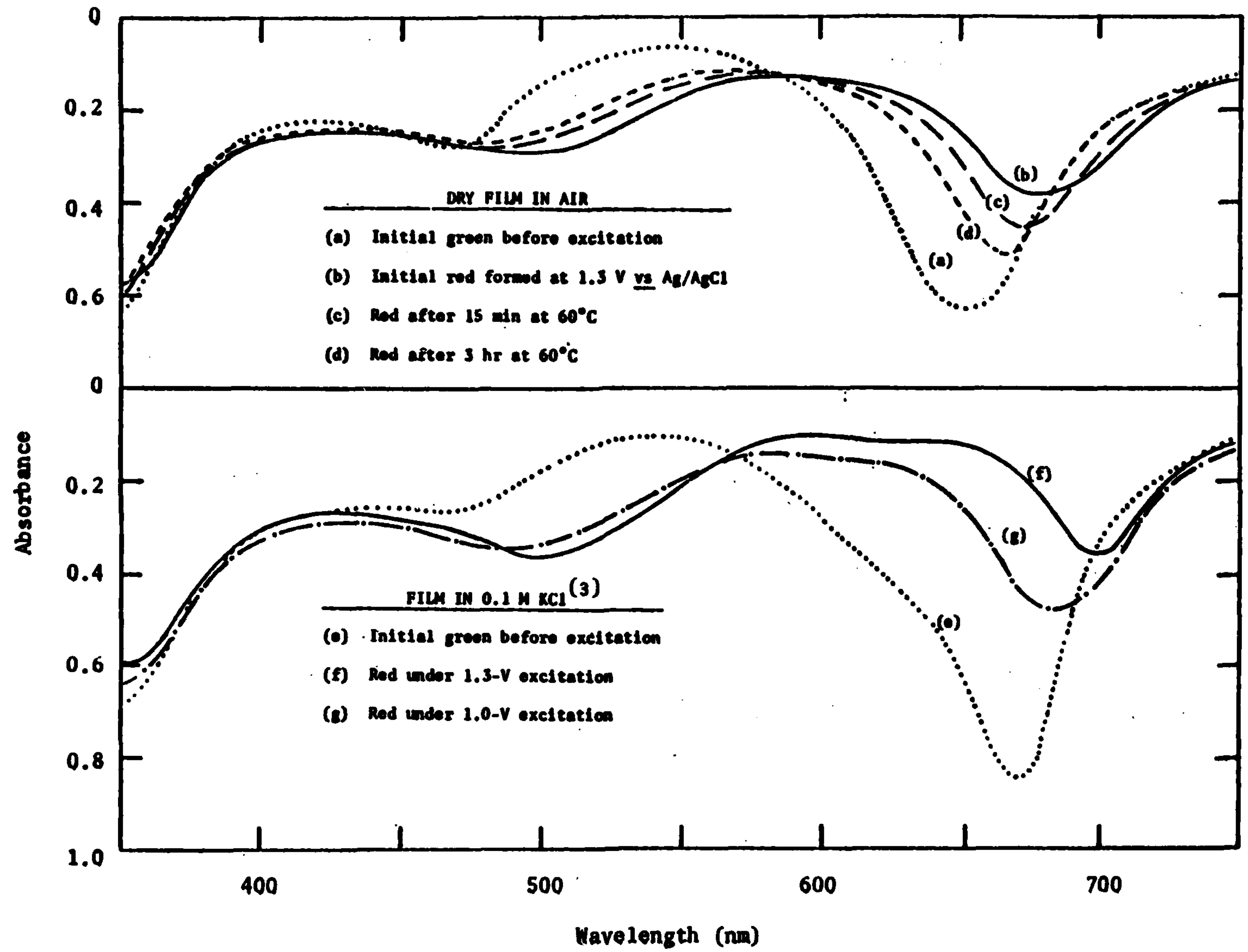

Figure 6. Absorption Spectra of Lutetium Diphthalocyanine Films under Several Conditions

With heating, the most prominent peak changed from a flat shape near 685 nm to a sharper form near 670 nm. The "final" spectrum in air, represented by Curve (d) of Figure 6, is different from that of the initial green dye deposit, represented by Curve (a).

The effect of temperature on the rate of color conversion of the dry films is evident from Figure 7, where the fraction converted, X, is expressed in terms of absorbances at 670 nm:

$$X = (A_t - A_i)/(A_f - A_i) \tag{1}$$

In Equation (1), A_i represents the initial absorbance, A_t the absorbance at time t, and A_f the final absorbance after prolonged heating in air. A plot of log (1-X) vs t for the data at 40°C was consistent with a first-order reaction of the red material. However, the data for the other temperatures were not sufficiently precise for this type of analysis to be made. It is apparent that most of the color change from the "initial red" state occurred within the first hour, except at room temperature. After two or three hours at elevated temperatures, the spectrum was not altered further by evacuation and exposure to helium in the glove box.

In some qualitative experiments, the red films were quickly dried in pure oxygen rather than air. Surprisingly, they became bright green. On subsequent exposure to air, the usual olive color appeared. No spectra were obtained in this sequence because of a malfunction of the spectrometer. One may speculate that two bright green forms of the dye can exist in the absence of an electrical signal, and that one of these becomes olive green on contact with water vapor in the air, while the other does not. The effects of oxygen will be more closely examined in future work.

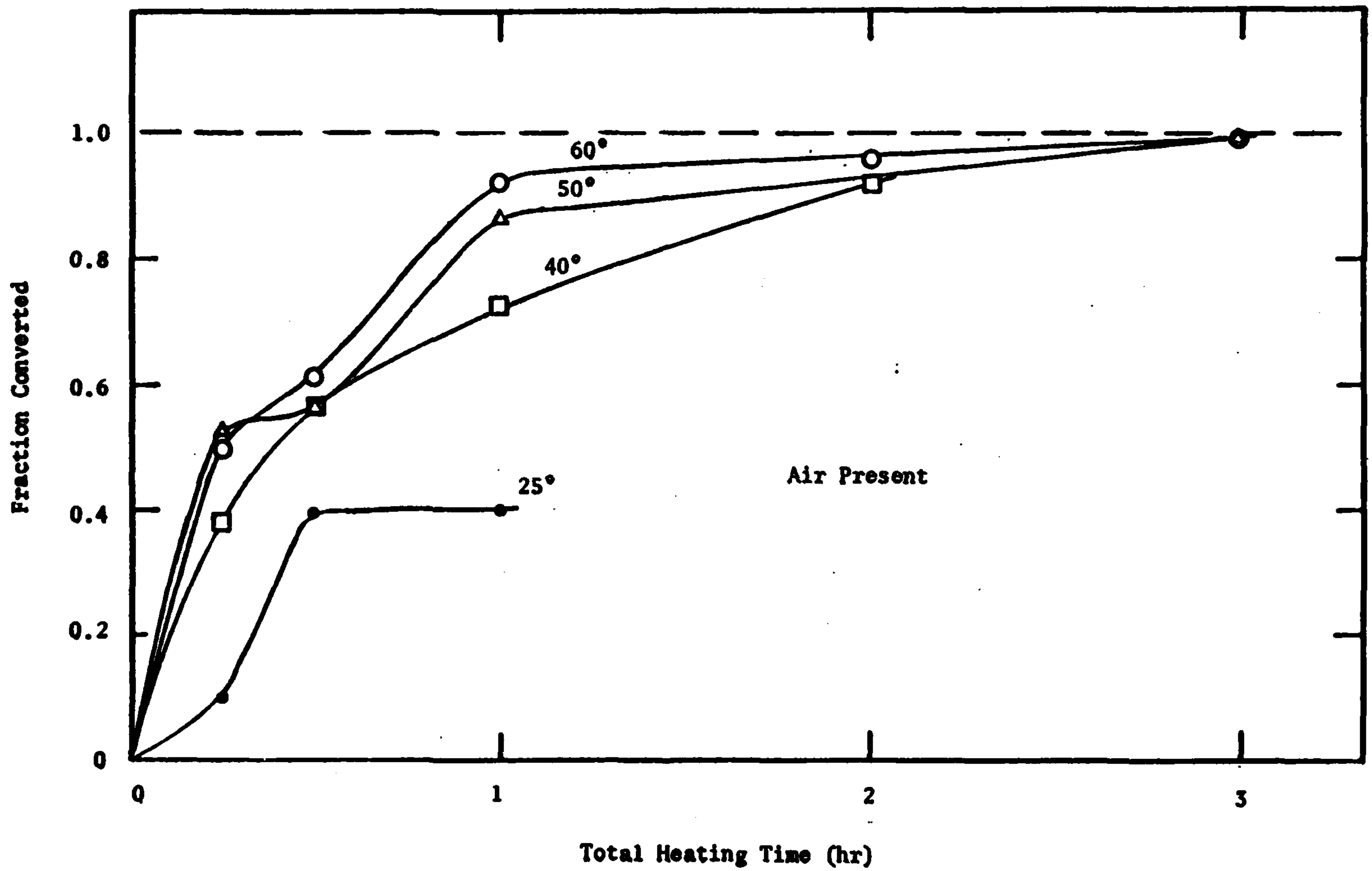

Figure 7. Temperature Dependence of Color Conversion in Dry Lutetium Diphthalocyanine Films

2. Moist Films with Various Anions on Insulating Substrates*

It was suspected from results of the chemical diagnostic experiments that lutetium diphthalocyanine could form more than one red oxidation product. This was later confirmed in the tracer study, which revealed stoichiometric quantities of the different electrolyte anions in the anodically formed red films.[8] The chloride-containing films on tin oxide could slowly change to green, as described above. It was also of interest to examine the stability of the anodic products on insulating substrates, where the chemistry of the fading process might be simpler.

For this purpose, green dye films were vacuum-deposited on single-crystal sapphire. A few were also prepared on Mylar. The electrolytes investigated were 1 M solutions of NaOAc (sodium acetate) KF, KCl, NaBr, KI, Na_2SO_4, and NaOOCϕ (sodium benzoate).

The films were converted to red forms by the boundary propagation technique used in the tracer study,[8] but for this work the cell was mounted inside a spectrometer during and after propagation. The first absorption spectrum was recorded for the green film with no liquid present. Electrolyte was then added to immerse the lower end of the film, and the red color was propagated upward from the meniscus by application of a constant anodic current. When the red section intercepted all of the incident light beam, the current was turned off, and spectra were recorded at intervals up to about 24 hr. Since the red film extended only a few millimeters above the liquid, it was in contact with moist air throughout the experiment.

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*Publication planned

The behavior of the dye films with the different anions fell into three classes:

(a) Low-voltage propagation with relatively fast return from red to green on cessation of the current (OAc^- and F^-).

This case is represented by the spectra in Figure 8, with isosbestic points clearly evident.

(b) Higher-voltage propagation with little or no spectral change of the red form in 24 hr (Cl^-, Br^-, and $SO_4^{=}$).

An example is given in Figure 9.

(c) No color propagation, even at the full compliance of the power supply (90 V) (I^- and ϕCOO^-).

For the red films that faded measurably, the spectra could be interpreted on the basis of a first-order reaction with

$$\ln (C/C_0) = -kt \qquad (2)$$

In Equation (2), C is the concentration of the red dye species at a time t following interruption of the current, C_0 is its initial concentration, and k is the first-order rate constant. The corresponding logarithmic plots are shown in Figure 10. Rate constants obtained from the slopes of these lines are given, with other data, in Table 5.

It is clear that the anion is a major factor determining the stability of the oxidation product. Since the film returns to the green state, the fading reaction is not simple hydrolysis; it must involve a chemical oxidation-reduction process. The tracer measurements showed a very gradual loss of chlorine content from the chloride film in ambient air.[8] Possible reactions to account for the color change in that case are:

$$LuH(Pc)_2 \cdot 2Cl \rightarrow LuH(Pc)_2 + Cl_2$$

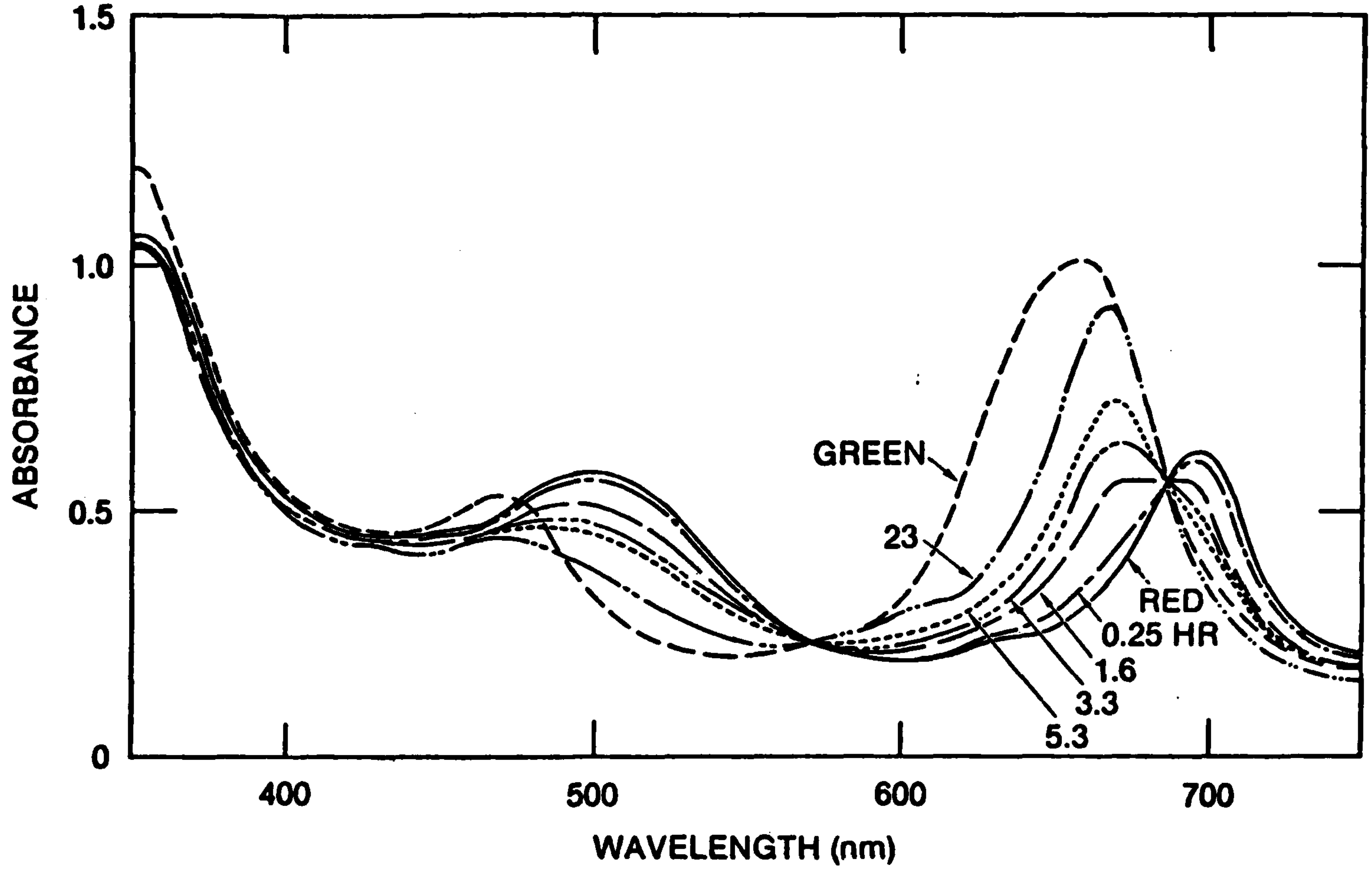

FIGURE 8. ABSORPTION SPECTRA OF LUTETIUM DIPHTHALOCYANINE FILM ANODICALLY OXIDIZED IN 1 M NaOAc.

[GREEN DENOTES ORIGINAL DYE FILM ON SAPPHIRE; RED DENOTES FRESHLY OXIDIZED FILM.]

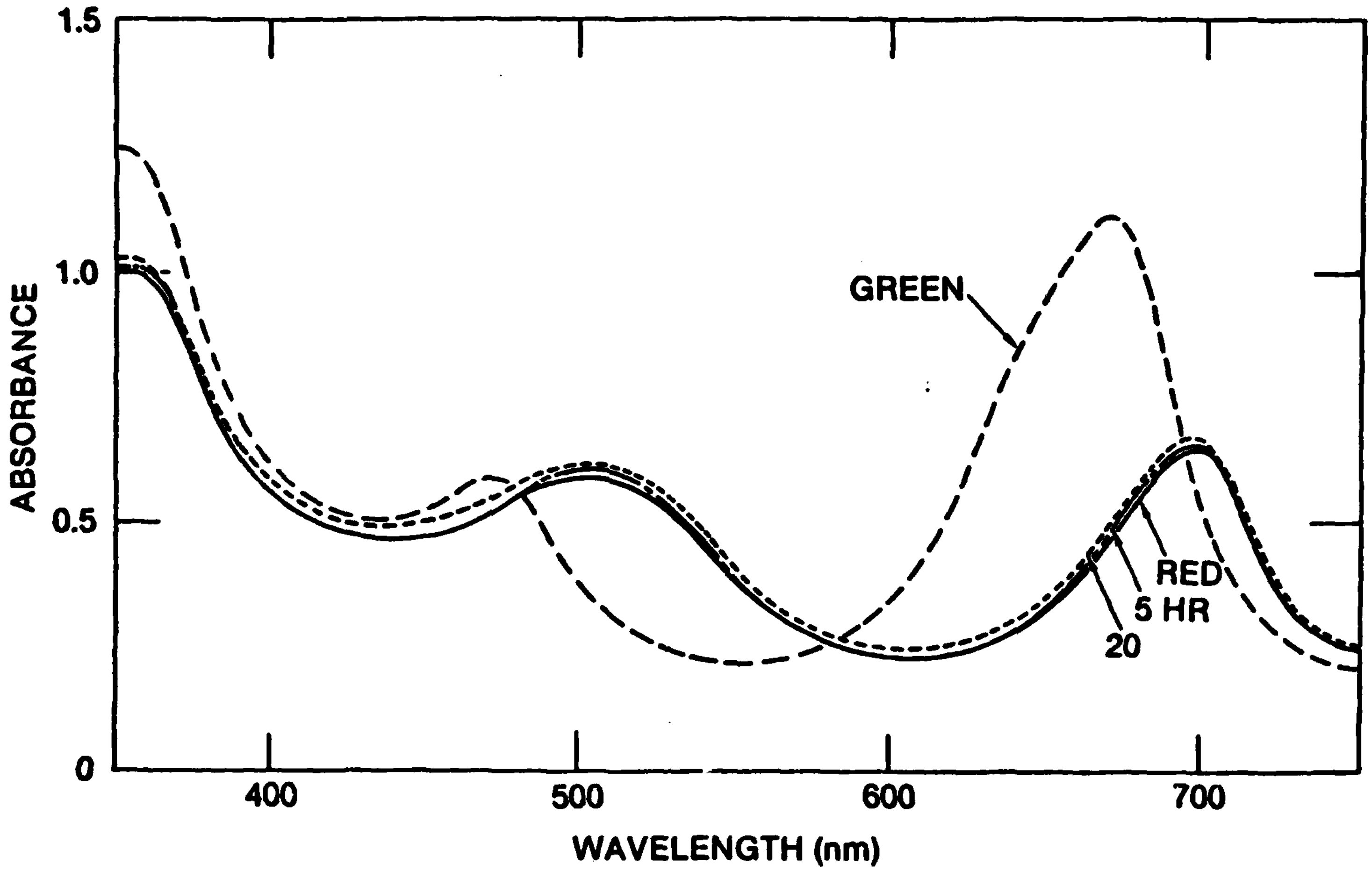

FIGURE 9. ABSORPTION SPECTRA OF LUTETIUM DIPHTHALOCYANINE FILM ANODICALLY OXIDIZED IN 1 M Na_2SO_4.

[GREEN DENOTES ORIGINAL DYE FILM ON SAPPHIRE; RED DENOTES FRESHLY OXIDIZED FILM.]

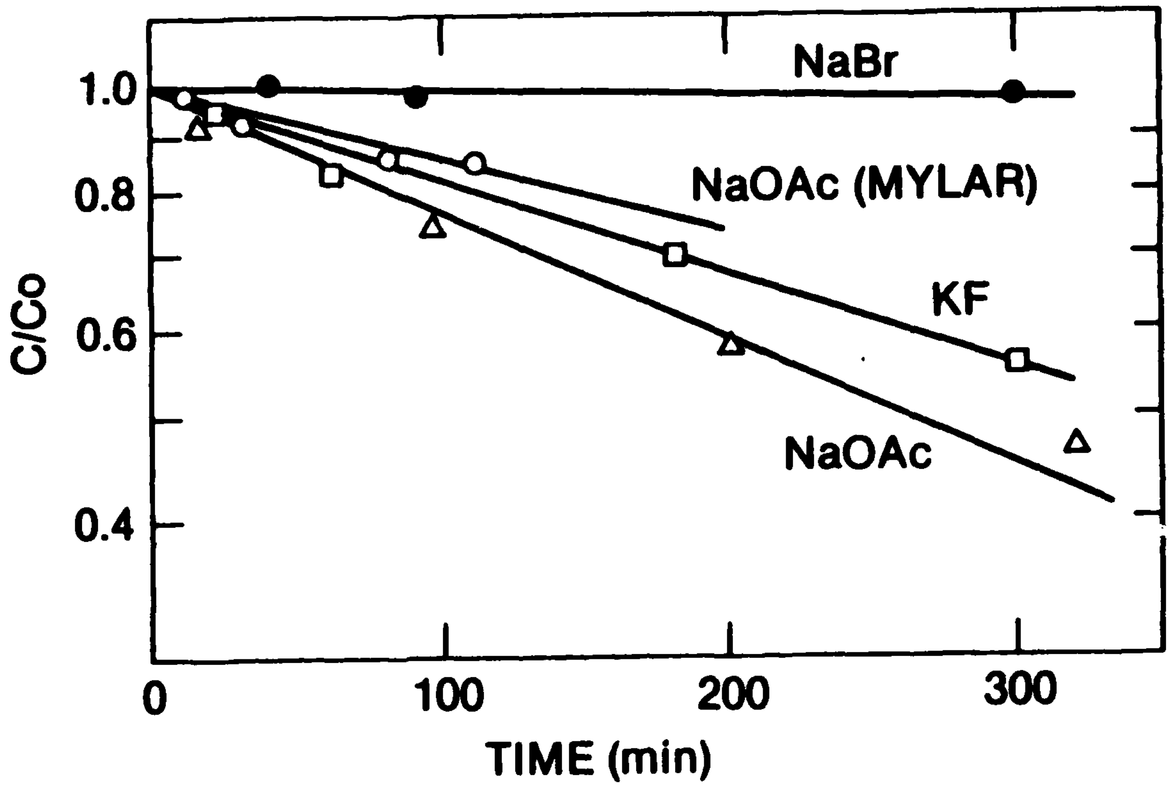

FIGURE 10. PLOTS FOR DETERMINATION OF FIRST-ORDER RATE CONSTANTS FOR OXIDIZED FILMS CONTAINING DIFFERENT ANIONS.

[ORDINATE IS $\log_{10}(c/c_0)$ FOR RED FORM OF DYE.]

TABLE 5

REACTION OF RATES OF RED FILMS CONTAINING DIFFERENT ANIONS[a]

Electrolyte[b]	A_{max} (Initial)	Current (μA)	k (hr^{-1})	Comments
NaOAc	1.01	2	0.16	
NaOAc	1.37	4	0.09	Mylar substrate.
KF	0.86	5	0.12	
KCl	1.00	3	----	Red form stable > 18 hr.
KCl	1.00	1	0.0039	Propagated from 0.011 M KCl; rate measured for dry film with tracer.[8]
NaBr	0.83	2	0.003	Estimated at 18 hr.
KI	0.88	5	----	No propagation above liquid.
Na_2SO_4	1.11	1 to 3	----	Red form stable > 20 hr in this study; dry film stable > 30 days[8].
NaOOCϕ	0.64	--	----	No propagation above liquid.

[a]Dye film on sapphire unless noted.

[b]1 M unless noted.

or $$LuH(Pc)_2 \cdot 2Cl + H_2O \rightarrow LuH(Pc)_2 + 2HCl + \tfrac{1}{2}O_2$$

Release of oxygen seems even more probable for the fluoride film, since the elemental halogen is extremely reactive. Further research is needed to characterize the reactions of the red films and the influences of oxygen, water, and the nature of the migrating anion.

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V. PUBLICATIONS

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1. F. A. Pizzarello and M. M. Nicholson, "Solid-State Anion Migration in the Anodic Oxidation of Lutetium Diphthalocyanine," J. Electron. Mat., 9, 231 (1980).

2. M. M. Nicholson and F. A. Pizzarello, "Galvanostatic Transients in Lutetium Diphthalocyanine Films," J. Electrochem. Soc., 127, 821 (1980).

PLANNED

1. F. A. Pizzarello and M. M. Nicholson, "Kinetics of Color Changes in Lutetium Diphthalocyanine Oxidation Products Containing Different Anions," Manuscript in preparation for Journal of the Electrochemical Society.

2. M. M. Nicholson and R. V. Galiardi, "Thin-Layer Electrochemical Cells Constructed from Precision-Etched Glass Cavities," Manuscript planned for Analytical Chemistry.

VI. PRESENTATIONS

1. M. M. Nicholson, "Diphthalocyanine Display Materials," Invited Paper, Gordon Research Conference on Thin Films, Tilton, New Hampshire, August 1978.

2. M. M. Nicholson, "Phthalocyanine Electrochromic Materials," Invited Paper, Abstract B-1, 21st Electronic Materials Conference, Boulder, Colorado, 1979.

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